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amendments.*(54) Title: PROCESS FOR PROTECTIVELY COATING ALUMINUM AND ITS ALLOYS AND COMPOSITE ARTICLES CONTAIN-
ING ALUMINUM AND ITS ALLOYS

(57) Abstract

Dilute solutions of (i) water-soluble resin made by reacting epoxy resins successively with amino-substituted aromatic carboxylic acids and amines or ammonia, (ii) a cross linking resin and (iii) surfactants provide a coating protective against corrosion on aluminum and its alloys that is suitable for use on structures such as heat exchangers that have multiple fins narrowly spaced from each other, without danger of bridging the spaces between fins.

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PROCESS FOR PROTECTIVELY COATING ALUMINUM AND ITS ALLOYS AND COMPOSITE ARTICLES CONTAINING ALUMINUM AND ITS ALLOYS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to processes for treating surfaces of aluminum and those of its alloys containing at least 45 % by weight of aluminum to form thereon relatively thin coatings that give excellent corrosion protection to the underlying metal. The invention is especially suited for application to composite metal structures that contain aluminum and its alloys along with at least one other metal, such as ordinary steel, galvanized steel, copper, and the like, with significantly different electrochemical characteristics from aluminum. A practically important example of this type of composite structure to which the invention is more particularly suited is a heat exchanger containing aluminum alloy fins and copper tubing on a galvanized steel support.

Statement of Related Art

A very wide variety of materials have been taught in the prior art for the general purposes of the present invention, but none of them has proved entirely satisfactory for all circumstances, particularly for heat exchangers with three different types of metal surfaces as described above. In such heat exchangers, the fins usually are set in close proximity to one another, making narrow gaps into which liquids with even moderately high

viscosity can penetrate only with difficulty. For many other types of metallic articles, a thick organic coating such as paint can be used to achieve good corrosion protection, but such coatings are generally unsuitable for heat exchangers, because (i) such coatings are usually applied as liquids with relatively high viscosity, giving rise to the difficulty of penetration into the narrow spaces between heat exchanger fins; (ii) even if such a coating can penetrate into narrow spaces, it often bridges them, thereby wasting some of the heat exchange surface needed; and (iii) a thick organic coating normally has poor heat conductance and therefore would unacceptably diminish the intended functioning of a heat exchanger if it covered the heat exchanger fins, even if the other difficulties could be avoided.

DESCRIPTION OF THE INVENTION

Objects of the Invention

A major object of this invention is to provide an organic coating composition and process that achieve at least one, and preferably as many as possible, of the following characteristics: good corrosion protection against most aqueous liquids, especially salt water, when applied in a thin enough coating to be suitable for heat exchanger fins; a low viscosity for application; minimization of variability of coating thickness when applied by conventional and economical means such as immersion and spraying to objects with complicated shapes; minimization of the use of volatile organic compounds ("VOC's") and/or hexavalent chromium and other materials that have been identified as environmentally damaging; durability; and reasonable cost. Another object is to provide cleaning and other auxiliary compositions and processes that are particularly useful in connection with the principal protective coating compositions and processes. Other and/or more specialized objects will be apparent to those skilled in the art from the description below.

General Principles of Description

Except in the claims and the operating examples, or where otherwise expressly indicated, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated is generally preferred. Also, unless expressly stated to the contrary: percent, "parts of", and ratio values are by weight; the term "polymer" includes "oligomer", "copolymer", "terpolymer", and the like; the description of a group or class of materials as suitable

or preferred for a given purpose in connection with the invention implies that mixtures of any two or more of the members of the group or class are equally suitable or preferred; description of constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description, and does not necessarily preclude chemical interactions among the constituents of a mixture once mixed; specification of materials in ionic form implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole (any counterions thus implicitly specified should preferably be selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counterions may be freely selected, except for avoiding counterions that act adversely to the objects of the invention); and the term "mole" and its variations may be applied to elemental, ionic, and any other chemical species defined by number and type of atoms present, as well as to compounds with well defined molecules.

Summary of the Invention

It has been found that aqueous solutions/dispersion of certain modified epoxy resins, which are described in general terms in U. S. Patent 4,098,744 of July 4, 1978 to Allen et al., when blended with cross linking resins and surfactants, provide satisfactory protective coatings, which do not substantially reduce heat transfer capabilities, for aluminum and its alloys containing at least 45 % of aluminum. Except to the extent that it may be inconsistent with any explicit statement herein, that part of the disclosure of U. S. Patent 4,098,744 appearing between column 2 line 16 and column 6 line 59 is hereby incorporated herein by reference, as is that part of the disclosure of U. S. Patent 4,119,609 of Oct. 10, 1978 to Allen et al. appearing between column 1 line 43 and column 5 line 43. More particularly, a process according to this invention provides a protective coating on a surface of aluminum or one of its alloys containing at least 45 % of aluminum and comprises steps of:

(A) forming on the surface to be coated a substantially uniformly thick film of an aqueous coating composition comprising, preferably consisting essentially of, or still more preferably consisting of, water and:

(A1) a water-soluble resin prepared by (a) reacting approximately chemically equivalent amounts of an epoxy resin having more than one 1,2-epoxy group per molecule and optionally also having one or more hydroxy

groups per molecule with an amino-containing aromatic carboxylic acid under conditions which cause the amino group of the aromatic carboxylic acid to react with the epoxy and/or hydroxyl groups of the epoxy resin but which leave the carboxyl groups of the aromatic carboxylic acid essentially unreacted, to produce an intermediate condensate and (b) solubilizing the intermediate condensate by reacting the pendant carboxyl groups with an amine or ammonia;

(A2) a cross linking resin selected from the group consisting of aminoplast and phenolic resins; and

(A3) a component of surfactant; and, optionally, one or more of:

(A4) silicone resin and

(A5) organic solvent for the epoxy resin before condensation;

(B) drying the liquid coating formed in step (A) to form a solid adherent coating on the surface to be protected; and, optionally,

(C) curing the solid coating formed in step (B) by heating it.

Description of Preferred Embodiments

In order to obtain maximum benefit from treatments according to this invention for forming a protective coating, it is strongly preferred to clean thoroughly the surface to be protected before forming over the surface the liquid coating of aqueous solution/dispersion of neutralized modified epoxy resin. Any cleaner known to be suitable for aluminum, and, if composite articles are to be protected, suitable also for the other metals present and desired to be protected, can be used satisfactorily in connection with a process according to this invention. Preferably, the cleaner composition, time of contact of the surface with the cleaner, and temperature of cleaner during such contact are chosen so that after cleaning and thorough rinsing with water, all the metal surfaces to be protected are free from "water-breaks", i.e., visually obvious variations in thickness of the water layer within a few millimeters of each other. Water-breaks are generally undesirable, as they give rise to at least the suspicion, and often to the fact, of non-uniform coating by subsequent treatments with aqueous liquids.

Several suitable commercially available cleaners are specified in the working examples below. In general moderately alkaline cleaners are preferred. More specifically, the pH value of a working cleaning solution used in connection with this invention pref-

erably is, with increasing preference in the order given, not less than 7.5, 8.0, 8.5, 9.0, 9.5, or 10.0 and independently preferably is not greater than 13.5, 13.0, 12.5, 12.0, or 11.5. Cleaners with high pH increase the danger of dissolving more of the aluminum surface being cleaned than is desirable, particularly when working with thin walled structures or those in which exacting dimensional tolerances must be maintained. On the other hand, if the pH is lower than desirable, the cleaning process will usually require a longer time to achieve a water-break free surface. Cleaners that are capable of achieving a water-break free surface (after subsequent rinsing with water) in, with increasing preference in the order given, not more than 90, 75, 60, 50, 40, 35, or 31 seconds, are preferred.

The concentration of non-volatile solids in a coating composition to be used according to this invention preferably is, with increasing preference in the order given, not greater than 19, 17, 15, 13, 11, 10, 9, 8, 7, 6.5, 6.1, 5.8, 5.5, 5.2, or 5.0 % and independently preferably is, with increasing preference in the order given, not less than 0.1, 0.2, 0.4, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, or 4.0 %.

The mass per unit area of the coating produced by the invention preferably is, with increasing preference in the order given, not less than 100, 200, 300, 400, 500, 600, 700, or 750 milligrams per square meter (hereinafter often abbreviated as "mg/m²") and independently preferably is, with increasing preference in the order given, not more than 4000, 2000, 1700, 1400, 1200, or 1100 mg/m².

The epoxy resin used to prepare the protective coating according to the invention preferably is a polymer of the diglycidyl ether of bis-phenol A, which is more systematically named "2,2-bis(4-hydroxyphenyl)propane" and may be abbreviated hereinafter as "BPA". Independently, the epoxide equivalent weight of the epoxy resin used preferably is, with increasing preference in the order given, not less than 200, 300, 350, 380, 400, 420, 430, or 445 and independently preferably is, with increasing preference in the order given, not more than 1500, 1400, 1300, 1200, 1100, 1000, 950, 900, 850, 800, or 760.

These preferred epoxy resin starting materials are normally solids at ambient temperature, and even when liquid at the temperature of condensation with the amino substituted aromatic carboxylic acids used to prepare the modified resin generally have very high viscosity. It is therefore preferred to dissolve the epoxy resin starting material in a suitable solvent before beginning the condensation reaction. Suitable solvents are giv-

en in the patents already incorporated by reference herein. It has been found that when a glycol monoether type of solvent is used, it not only is a satisfactory solvent for the condensation reaction but may be left in the composition to be coated on an aluminum surface to be protected without adverse effects on performance. Solvents of this type are therefore preferred. If desired, of course, the solvent may be removed from the composition before coating it on an aluminum surface to be protected, but ordinarily there appears to be no benefit from introducing this extra step into the process.

The most preferred neutralizing amine for making the resins in a protective coating according to this invention is dimethylethanolamine, which may be abbreviated hereinafter as "DMEA".

Aminoplast resins are preferred over phenolic resins as cross linking agents for preparing the liquid compositions to be used as coatings for this invention, and among the aminoplast resins melamine-formaldehyde resins are preferred over urea-formaldehyde resins. The ratio of non-volatile solids from melamine-formaldehyde resin to solids derived from epoxy resin in the modified epoxy resin prepared by reaction with amino-substituted aromatic carboxylic acids preferably is, with increasing preference in the order given, at least 0.5, 1.0, 1.5, or 2.0 % and independently preferably is, with increasing preference in the order given, not greater than 100, 75, 50, 45, 41, 38, or 36 %. Either water dilutable cross linking resins added after dilution of the modified epoxy resin with water or less water tolerant cross linking resins added to a more concentrated modified epoxy resin dispersion can equally well be used.

A coating composition to be used according to this invention preferably contains a component of surfactant molecules, preferably in an amount such that the ratio of the amount of total surfactant to the total of epoxy resin and amino-substituted aromatic carboxylic acids reacted to make the coating composition is, with increasing preference in the order given, not less than 0.1, 0.4, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, or 1.3 % and independently preferably is, with increasing preference in the order given, not more than 10, 5, 4, 3, 2.5, 2.1, 1.8, 1.6, or 1.5 %. Independently, the surfactant component preferably includes two chemically distinct types of surfactants: (i) a fluorinated surfactant, preferably consisting predominantly of fluorinated alkyl esters, and (ii) a non-fluorine-containing alcohol terminated alkylaryl ethoxylate, most preferably an ethoxylate of nonyl phenol with an average of 9 ethylene oxide molecules per phenol molecule. Independently, the

ratio of the amount of surfactant type (i) as defined immediately above to the amount of surfactant type (ii) that is present in the coating compositions according to the invention preferably is, with increasing preference in the order given, not less than 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.73, 0.75, or 0.77 and independently preferably is, with increasing preference in the order given, not more than 10, 9, 8, 7, 6, 5, 4, 3, 2.5, 2.1, 1.8, 1.5, 1.2, 1.1, 1.0, 0.95, 0.90, 0.85, 0.83, or 0.81.

In general, it is preferred to include the optional silicone resin component in a coating composition used according to this invention. When used, the amount of silicone resin preferably is such that the ratio of the amount of silicone resin to the total of epoxy resin and amino substituted aromatic carboxylic acid condensed to make the modified resin used in a coating according to this invention is, with increasing preference in the order given, not less than 0.001, 0.002, 0.003, 0.004, 0.0045, 0.0048, 0.0050, or 0.0052 and independently preferably is, with increasing preference in the order given, not greater than 0.05, 0.04, 0.03, 0.02, 0.01, 0.009, 0.008, 0.007, 0.0065, 0.0061, 0.0059, or 0.0057.

In a process according to the invention, the coating step is normally performed at ambient temperature (20 - 25 ° C) for convenience, but may be performed at any temperature at which the coating composition is liquid, e.g., from 10 - 90 ° C. The liquid film formed on the surfaces to be protected may be dried simply by exposure to air and preferably is allowed at least to drain in air for a few minutes immediately after removing the coated surface from contact with the bulk of the coating composition, in order to promote uniformity of thickness of the liquid film on the entire surface to be protected. Normally, however, after at most 15 minutes, more often at most 5 minutes of draining, drying is hastened by the use of higher temperatures, particularly because it is preferable to cure as well as to dry the coating. Therefore the steps of a process according to the invention that follow the formation of a liquid film preferably include a time of exposure of the coated surface to a temperature that is, with increasing preference in the order given, at least 100, 110, 120, 130, 140, 145, 150, 155, 158, 161, 163, or 165 ° C and independently preferably is, with increasing preference in the order given, not greater than 250, 240, 230, 220, 210, 200, 197, 195, 193, or 191 ° C for a time interval that preferably is, with increasing preference in the order given, at least 0.5, 1.0, 2.0, 4, 8, 15, or 25 minutes and independently preferably is, with increasing preference in the order given, not greater than 300, 150, 75, 60, 50, 40, 35, or 31 minutes.

The practice of this invention may be further appreciated by consideration of the following, non-limiting, examples.

Evaluation of Cleaners for Use Prior to Protective Coating

Cleaner Test 1

5 PARCO® 2960 Cleaner concentrate was diluted with tap water to make a 20 % solution of the concentrate, which was heated to 46 - 49 ° C. A sample of heat exchanger array containing both copper and aluminum was immersed in this solution for 30 seconds, then rinsed for 2 minutes with tap water spray. The aluminum part of the immersed sample was mostly covered with water-breaks. A separate aluminum panel was similarly
10 immersed in the same solution for the same time and also had water breaks after rinsing. The aluminum panel was returned to the cleaner solution for 3 minutes immersion, followed by another 2 minute rinse with tap water, but still only 80 - 85 % of the surface was free of water-breaks. The heat exchanger sample was then returned to the hot solution for an additional 4.5 minutes immersion, followed again by a 2 minute water rinse.
15 This length of cleaning treatment eliminated visible water-breaks, but the surface felt slightly slimy to the touch. Neither the aluminum nor the copper was noticeably discolored.

Cleaner Test 2

P3® Hot Stripper 52 was diluted with tap water to a 20 % solution. This solution,
20 at either 64 or 82 ° C, produced water-break free surfaces on either aluminum panels or composite aluminum and copper samples after 30 seconds immersion in the cleaning solution, followed by 2 minutes rinse with tap water.

Cleaner Test 3

RIDOLINE® 53 C Cleaner concentrate was diluted with tap water to give a solution containing 15 grams per liter ("g/L") of the concentrate. The solution was main-
25 tained for testing at 62° C. This solution produced water-break free surfaces on aluminum panels, composite aluminum and copper samples, and on galvanized steel samples after 30 seconds immersion in the cleaning solution, followed by 2 minutes rinse with tap water. No discoloration of aluminum, copper, or galvanized steel was visually observable after as much as 5 minutes of immersion in the hot cleaning solution.
30

Cleaner Test 4

RIDOLINE® 336 Cleaner concentrate was diluted with tap water to give a solu-

tion containing 19.9 g/L of the concentrate. The solution was maintained for testing at 54 to 57 ° C. This solution produced water-break free surfaces on aluminum panels, composite aluminum and copper samples, and on galvanized steel samples after 30 seconds immersion in the cleaning solution, followed by 2 minutes rinse with tap water. No
5 discoloration of aluminum, copper, or galvanized steel was visually observable after as much as 5 minutes of immersion in the hot cleaning solution.

Cleaner Test 5

PARCO® 305 Cleaner concentrate was diluted with tap water to make a 2 % by volume solution of the concentrate, which was maintained at 54 - 57 ° C. A sample of
10 heat exchanger array containing both copper and aluminum was immersed in this solution for 30 seconds, resulting in immediately obvious gas evolution, presumably of hydrogen, from the aluminum part of the immersed sample, then rinsed for 2 minutes with tap water spray. The aluminum part of the immersed sample had a milky-appearing surface upon removal from the cleaner solution but was water-break free after rinsing. Cop-
15 per, aluminum and galvanized steel surfaces all remained free from discoloration by this solution after at least 5 minutes immersion.

Cleaner Test 6

P3®-T V 5220-1 Cleaner concentrate was diluted with tap water to a 7 % solution, which was maintained for testing at 54° C. Immersion of an aluminum panel or of
20 a copper-aluminum composite sample for 30 seconds, followed by 2 minutes rinse with tap water, was not sufficient to produce aluminum surfaces free from water-breaks, but an additional 1.5 minutes of immersion did provide water-break free aluminum surfaces on both types of substrates, and there was no visual evidence of discoloration or other damage any of aluminum, copper, and galvanized steel.

25 PARCO® 2960 Cleaner concentrate, P3® Hot Stripper 52, RIDOLINE® 53 C Cleaner concentrate, RIDOLINE® 336 Cleaner concentrate, PARCO® 305 Cleaner concentrate, and P3®-T V 5220-1 Cleaner concentrate are all commercially available from the Parker Amchem Division of Henkel Corporation, Madison Heights, Michigan. All of them except the last are moderately to strongly alkaline cleaners, and the last named
30 is neutral or nearly neutral.

Preparation of Modified Epoxy Resins in Aqueous Solution/Dispersion

Resin Example 1

An amount of 413 grams (hereinafter usually abbreviated "g") of EPON™ Resin 1001 F, commercially available from Shell Chemical Co. and described by its supplier as a polymer of the diglycidyl ether of BPA with an epoxide equivalent weight of 450 - 550, was charged to a two liter capacity resin kettle equipped with a stainless steel bladed mechanical stirrer, reflux condenser, inlet port, heating mantle, temperature monitor and controller, and means for maintaining a nitrogen atmosphere over the liquid part of the contents of the kettle. Then 160 g of PROPASOL™ P solvent (hereinafter denoted briefly as "P Solvent"), commercially available from Union Carbide Corp. and reported by its supplier to be "n-propoxyl propanol", was added to dissolve the resin and produce a mixture with practically manageable viscosity. This mixture was heated with stirring to 68 - 69 ° C and held there overnight with stirring, then raised in temperature to 83 - 85 ° C, and then 57 g of solid powdered p-aminobenzoic acid ("PABA") was added with continued stirring. An additional 20 g of P Solvent was then used to wash all the solid PABA into the kettle. The temperature was raised to 115 - 119 ° C and held there for 9 hours, with the temperature maintained within the range 116 - 117 ° C for the last 6 hours of this interval. Immediately after this 33 g of DMEA was added to the mixture, which was then stirred for 5 minutes. Then, a mixture of 3.8 g of FLUORAD™ FC-430 (briefly denoted hereinafter as "FC-430"), a surfactant commercially available from Minnesota Mining and Manufacturing Co. and described by its supplier as "fluorinated alkyl esters", with 3.1 g of IGEPAL™ CO-630 (briefly denoted hereinafter as "CO-630"), another surfactant commercially available from Rhône-Poulenc and described by its supplier as non-ylphenoxypoly(ethyleneoxy)ethanol with an average of eight ethyleneoxy groups per molecule, which had been previously warmed in a microwave oven to reduce its viscosity, was added. Following this, 144 g of CYMEL™ 303 melamine-formaldehyde resin (briefly denoted hereinafter as "303 Resin"), commercially available from American Cyanamid Corp. and described by its supplier as "hexamethoxy methylmelamines", which had been previously warmed in a hot water bath to reduce its viscosity, was added. (A hot air blower was used to force any visible amount of these added viscous materials that had adhered to the sides of the inlet port or reactor to fall into the main mixture.) Once the addition of the 303 Resin was complete, the stirrer was turned off and the heating

mantle dropped so that the mixture could cool overnight.

The mixture as thus prepared and conditioned was reheated to 90 - 95 ° C and stirring was resumed. 500 milliliters ("mL") of deionized water (hereinafter briefly denoted as "DIW") was then added dropwise, sufficiently slowly that the stirring motor did not slip. The entire mixture was then transferred to a vessel with 4 liters capacity and a high-shear agitator, which was kept in operation, with the temperature of the agitated mixture being maintained at about 75° C, during continued dropwise addition of deionized water until a total of 1726 mL had been added. Cooling of the mixture was then begun, and during this cooling an additional 254 g of deionized water was added dropwise as the mixture cooled to ambient temperature of about 22° C. A total of 1577 g of coating composition concentrate, with a solids content of 31.7 % (average of four samples) as determined by microwave drying of about 1 g samples, was recovered.

Resin Example 2

An amount of 243 g of EPON™ Resin 1001 F was charged to a one liter capacity resin kettle equipped with a stainless steel bladed mechanical stirrer, reflux condenser, inlet port, heating mantle, temperature monitor and controller, and means for maintaining a nitrogen atmosphere over the liquid part of the contents of the kettle. Then 114 g of P Solvent was added to dissolve the resin and produce a mixture with practically workable viscosity. This mixture was heated with stirring to 82° C, and then 34 g of solid powdered PABA was added with continued stirring. An additional 20 g of P Solvent was finally used to wash all the solid PABA into the kettle. During the addition of PABA, the temperature was raised to 116° C and held between that temperature and 118° C for 9 hours. Immediately after this 19.3 g of DMEA and 12.2 g of 303 Resin were added to the mixture, which was then stirred for 10 minutes, then allowed to cool overnight.

The mixture prepared as described immediately above was warmed to 95° C and transferred to an open top 2 liter capacity stainless steel beaker equipped with a Cowles blade mixer. (The mass of the resin mixture transferred was 359 g, indicating evaporation of a total of about 84 g of material from the mixture.) Then a mixture of 3.1 g of BYK™ 301, commercially available from Byk-Mallinckrodt Chemische Produkte GmbH, U. S. Marketing Div., Melville, New York and described by its supplier as a 50 % solution of a "special, paint-compatible silicone resin useful to increase slip properties", 2.4 g of FC-430, and 1.8 g of CO-630, which had been previously warmed in a mi-

crowave oven to reduce its viscosity, was added with stirring. During stirring, the temperature fell to 49 - 55 ° C and was maintained in that range during the subsequent addition of DIW. The first 200 g portion of the DIW added was added very slowly because the mixture was very viscous, and even after the viscosity began to drop, indicating conversion to a resin-in-water dispersion, the addition of water was kept to only a moderate rate in order to avoid lumping. Enough DIW was added to result in a total of 1153 g of finished resin solution/dispersion, having a pH of 8.46 and a solids content of 22.0 %, with about 3.8 % of the total solids being from the amount of 303 Resin added.

Resin Example 3

An amount of 492 g of EPON™ Resin 1002 F, commercially available from Shell Chemical Co. and reported by its supplier to be a polymer of the diglycidyl ether of BPA with an epoxide equivalent weight of 650 - 750, was charged to a one liter capacity resin kettle equipped with a stainless steel bladed mechanical stirrer, reflux condenser, inlet port, heating mantle, temperature monitor and controller, and means for maintaining a nitrogen atmosphere over the liquid part of the contents of the kettle, and the resin and gas space of the resin kettle were purged with nitrogen gas. Then 191 g of P Solvent was added to dissolve the resin and produce a mixture with practically workable viscosity. This mixture was heated with stirring to about 85° C and held at that temperature for about 10 minutes, and then 56 g of solid powdered PABA was added with continued stirring. An additional 10 g of P Solvent was finally used to wash all the solid PABA into the kettle. During the addition of PABA, the temperature was raised to 115° C and held between that temperature and 120° C for 9 hours. Immediately after this 36 g of DMEA was added with stirring, followed by 6.2 g of BYK™ 301 silicone resin, 4.5 g of FC-430, and 3.7 g of CO-630 over a period of 15 minutes. Then 49.4 g of 303 Resin was added to the mixture, which was then stirred for 15 minutes, then allowed to cool overnight.

The mixture prepared as described immediately above, having a residual mass of 745 g, was warmed to 95° C and transferred to an open top 4 liter capacity stainless steel beaker equipped with a Cowles blade mixer. Then DIW at a temperature of 60 - 65 ° C was slowly added and mixed into the initial charge of resin to convert it to a resin-in-water dispersion. Enough DIW was added to result in a total of 1808 g of resin, which was cooled to ambient temperature of about 22° C, after which an additional 264 g of DIW was added to reduce the viscosity and produce 2072 g of resin solution/dispersion. Be-

cause the presence of some solid lumps was noted, this intermediate was filtered through a conventional paint filter to produce 2019 g of final filtered liquid resin solution/dispersion having a pH of 8.74 and a solids content of 26.4 %.

Resin Example 4

5 An amount of 826 g of EPON™ Resin 1001 F was charged to a two liter capacity resin kettle equipped with a stainless steel bladed mechanical stirrer, reflux condenser, inlet port, heating mantle, temperature monitor and controller, and means for maintaining a nitrogen atmosphere over the liquid part of the contents of the kettle. Then 360 g of P Solvent was added to dissolve the resin and produce a mixture with practically workable
10 viscosity. The condenser water was then turned on, the liquid and gas spaces purged with nitrogen, and stirring begun. This mixture was heated with stirring to 84° C, at which point dissolution of the EPON™ Resin appeared to be complete. Then 114 g of solid powdered PABA was added over a 10 minute period with continued stirring. An additional 20 g of P Solvent was then used to wash all the solid PABA into the kettle.
15 The temperature was raised to 115 - 120 ° C and held there for 9 hours. Immediately after this 66 g of DMEA, 10.4 g of BYK™ 301, 7.5 g of FC-430, and 6.1 g of CO-630 were added in order. Following this, 289 g of 303 Resin was added. Once the addition of the 303 Resin was complete, the stirrer was turned off and the heating mantle dropped so that the mixture could cool overnight.

20 The mixture as thus prepared and conditioned, having a residual mass of 1549 g, was reheated to 90 - 95 ° C and then transferred to a vessel with 4 liters capacity and a high-shear agitator, which was kept in operation, with the temperature of the agitated mixture being maintained at about 75° C, during addition of a total of 4648 g of warmed DIW. Until apparent inversion had occurred after the addition of about 2245 g of DIW,
25 the DIW was added slowly, but afterward it was added rapidly. The product was then filtered as in Resin Example 3 to produce 5648 g of final modified resin solution/dispersion having a pH of 8.75 and a solids content of 20.8 %.

Coatings

Group 1

30 Rectangular test panels 10 × 15 cm in size were cut from Type 3003 aluminum alloy. These panels were cleaned by immersion in a cleaner solution prepared as described in Cleaning Test 3 above and maintained at a temperature of 60° C during use.

All panels in this Group were initially cleaned by immersion for 30 seconds in this cleaning solution, followed by a 2.5 minute spray tap water rinse. Coating Composition 1.1 was made by mixing 505 g of DIW with 93 g of the product of Resin Example 1 above. Test Panel 1.1.1 was prepared by immersing a cleaned and rinsed panel as described
5 above for 30 seconds in Coating Composition 1.1 at a temperature of 20 - 25 ° C, removing the panel from contact with Coating Composition 1.1 and allowing the panel to drip in open air for 5 - 10 minutes, then drying and curing the panel in an oven at 177° C for 30 minutes. Test Panel 1.1.2 was prepared in the same manner, except that the time of immersion in Coating Composition 1.1 was 60 seconds.

10 Coating Composition 1.2 was prepared by adding 1.2 g of BYK™ 301 silicone resin to the remaining quantity of Coating Composition 1.1. Test Panels 1.2.1 and 1.2.2 were then prepared in the same manner as Test Panels 1.1.1 and 1.1.2 respectively, except for substituting Coating Composition 1.2 for Coating Composition 1.1. Coating Composition 1.3 was prepared by mixing 9.5 g of 30 % H₂O₂ in water solution with 568
15 g of Coating Composition 1.2. Test Panels 1.3.1 and 1.3.2 were then prepared in the same manner as Test Panels 1.1.1 and 1.1.2 respectively, except for substituting Coating Composition 1.3 for Coating Composition 1.1. Comparison Test Panel 1.1 was prepared in the same manner as Test Panel 1.1.1, except for omitting the contact with Coating Composition 1.1.

20 Group 2

For this group, the same type of test panels as for Group 1 were cleaned by immersion in a cleaner solution prepared as described in Cleaning Test 6 above and maintained at a temperature of 60° C during use. All panels in this Group were initially cleaned by immersion for 2 minutes in this cleaning solution, followed by a 2 - 2.5 min-
25 ute spray tap water rinse. Coating Composition 2.1 was the same composition as Coating Composition 1.3 above. Test Panel 2.1.1 was prepared by immersing a cleaned and rinsed panel as described above for 30 seconds in Coating Composition 2.1 at a temperature of 20 - 25 ° C, removing the panel from contact with Coating Composition 2.1 and allowing the panel to drip in open air for 5 - 10 minutes, then drying the panel in an oven
30 at 177° C. Test Panel 2.1.2 was prepared in the same manner, except that the time of immersion in Coating Composition 2.1 was 60 seconds. Comparison Test Panel 2.1 was prepared in the same manner as Test Panel 2.1.1, except for omitting the contact with

Coating Composition 2.1. Coating Composition 2.2 was made by mixing 2479 g of DIW with 396 g of the product of Resin Example 1 above, resulting in a product with a pH of 8.99. Test Panels 2.2.1 and 2.2.2 were prepared in the same manner as Test Panels 2.1.1 and 2.1.2 respectively, except for substituting Coating Composition 2.2 for Coating Composition 2.1.

Comparison Group 3

For this group, the same type of test panels as for Group 1 were cleaned by immersion in a cleaner solution as used for Group 1 and subsequent rinsing, and then were immersed in an aqueous solution containing 0.10 % of a polymer made substantially as described in column 11 lines 47 - 59 of U. S. Patent 5,068,299 of Nov. 26, 1991 to Lindert et al. and 0.022 % of fluozirconic acid, a solution hereinafter denoted as "T-13", instead of in Coating Solution 1. Except for this change in coating solution, Comparison Test Panels 3.1.1 and 3.1.2 were prepared in the same manner as Test Panels 1.1.1 and 1.1.2 respectively.

Group 4

In this group, specimens cut from actual heat exchangers and containing a plurality of aluminum alloy fins spaced apart the same distance as they would be in a typical practical heat exchanger were tested instead of flat panels as in the previous Groups. Coating Composition 4.1 was prepared by mixing 2479 g of Coating Composition 2.2 with 4.9 g of BYK™ 301 silicone resin. Except for the substitution of Coating Composition 4.1 for another coating composition and for substituting vigorous shaking by hand for allowing the coated substrate to drip, Test Parts 4.1.1 and 4.1.2 were prepared in the same manner as Test Panels 1.1.1 and 1.1.2 respectively. There was no evidence of bridging on the Test Parts.

Group 5

In this group, a pretreatment with TD 1355 CU was used before coating with a modified epoxy resin. The pretreatment consisted of 30 seconds of immersion of test panels as described above in T-13, followed immediately after removal by further treatment in the same manner as for Test Panels 1.1.1 and 1.1.2. Corresponding Test Panel Numbers for panels with the pretreatment were 5.1.1 and 5.1.2 respectively.

Group 6

Coating Composition 6.1 was prepared by adding sufficient dimethylethanolam-

ine to Coating Composition 1.1 to raise the pH value to 9.71. Test Panels 6.1.1, 6.1.2, 6.1.3, and 6.1.4 were prepared by substituting this coating composition, but otherwise in the same manner, as for Test Panels 1.1.1, 1.1.2, 2.1.1, and 2.1.2 respectively.

Group 7

5 Coating Composition 7.1 was made by mixing 22 g of DIW with 68 g of the product from Resin Example 2. Test Panel 7.1.1 of Type 3003 Aluminum Alloy was made in the same manner, except for substituting Coating Composition 7.1, as Test Panel 1.1.2. Coating Composition 7.2 was made by adding to Coating Composition 7.1 a sufficient amount of CYMEL™ 385 Resin (hereinafter briefly denoted as "385 Resin"), a product
10 commercially available from American Cyanamid Co., Wayne, New Jersey and described by its supplier as a "partially methylated, melamine-formaldehyde cross-linking agent that has a low degree of alkylation and is infinitely dilutable with water" and contains 80 ± 2 % solids, to supply an amount of active melamine-formaldehyde resin ingredient equal to that already present in Coating Composition 7.1 from the CYMEL™
15 303 Resin used in preparing the product of Resin Example 2. Test Panel 7.2.1 was then made in the same manner as Test Panel 7.1.1, except that Coating Composition 7.2 was substituted for Coating Composition 7.1. By adding additional amounts of 385 Resin, Coating Compositions 7.3, 7.4, 7.5, and 7.6 containing respectively 3, 4, 5, and 6 times the amount of active melamine-formaldehyde resin in Coating Composition 7.1 were prepared
20 in the same manner, and, except for substituting the corresponding Coating Compositions, Test Panels 7.3.1, 7.4.1, 7.5.1, and 7.6.1 were prepared in the same manner as Test Panel 7.1.1.

Group 8

Coating Composition 8.1 was prepared by mixing 243 g of DIW with 57 g of the
25 product from Resin Example 3. Coating Compositions 8.2, 8.3, 8.4, and 8.5 were then made by adding 385 Resin in the same manner as described in Group 7 so as to produce respectively 1.5, 2.0, 2.5, and 3.0 times the total concentration of active melamine-formaldehyde resin that is present in Coating Composition 8.1. Test Panels 8.1.1, 8.2.1, 8.3.1, 8.4.1, and 8.5.1 were then made with these Coating Compositions in the same manner
30 as otherwise specified in Group 7.

Tests and Results

Most of the coated panels and parts prepared as described above were tested for salt spray corrosion resistance according to American Society for Testing and Materials ("ASTM") Standard Method B 117-61 after 1000 hours of salt spray exposure. Results are shown in Table 1.

TABLE 1

Test Sample Identification	Results
Panels: 1.1.1	No evidence of corrosion
1.1.2	No evidence of corrosion
1.2.1	No evidence of corrosion
1.2.2	No evidence of corrosion
1.3.1	No evidence of corrosion
1.3.2	No evidence of corrosion
2.1.1	No evidence of corrosion
2.1.2	No evidence of corrosion
2.1.3	Considerable discoloration; white rust
2.2.2	Some discoloration
3.1.1	Discoloration and some white rust
3.1.2	Discoloration and some white rust
5.1.1	No evidence of corrosion
5.1.2	No evidence of corrosion
6.1.1	No evidence of corrosion
6.1.2	No evidence of corrosion
6.1.3	No evidence of corrosion
6.1.4	No evidence of corrosion
7.1.1	No evidence of corrosion
7.2.1	No evidence of corrosion
7.3.1	No evidence of corrosion

... Table continued on next page ...

Test Sample Identification	Results
7.4.1	No evidence of corrosion
7.5.1	No evidence of corrosion
7.6.1	No evidence of corrosion
8.1.1	No evidence of corrosion
8.2.1	No evidence of corrosion
8.3.1	No evidence of corrosion
8.4.1	No evidence of corrosion
8.5.1	No evidence of corrosion
<u>Parts:</u> 4.1.1	Corrosion at aluminum/copper junctions; no evidence of corrosion on aluminum fin surfaces
4.1.2	Corrosion at aluminum/copper junctions; no evidence of corrosion on aluminum fin surfaces

The invention claimed is:

1. A process of providing a protective coating on a surface of aluminum or one of its alloys containing at least 45 % of aluminum, said process comprising the steps of:

(A) forming on the surface to be coated a substantially uniformly thick film of an aqueous coating composition consisting essentially of water and:

(A1) a water-soluble resin prepared by (a) reacting approximately chemically equivalent amounts of an epoxy resin having more than one 1,2-epoxy group per molecule and optionally also having one or more hydroxy groups per molecule with an amino-containing aromatic carboxylic acid under conditions which cause the amino group of the aromatic carboxylic acid to react with the epoxy and/or hydroxyl groups of the epoxy resin but which leave the carboxyl groups of the aromatic carboxylic acid essentially unreacted, to produce an intermediate condensate and (b) solubilizing the intermediate condensate by reacting the pendant carboxyl groups with an amine or ammonia;

(A2) a cross linking resin selected from the group consisting of aminoplast and phenolic resins; and

(A3) a component of surfactant; and

(B) drying and curing the liquid coating formed in step (A) to form a solid adherent coating on the surface to be protected, said drying and curing including a period of at least 2 minutes during which the dried film is exposed to a temperature of at least 100° C.

2. A process according to claim 1, wherein the amino-containing aromatic carboxylic acid is an amino-substituted benzoic acid, the intermediate condensate is solubilized by reaction with a tertiary amine, the cross linking resin is selected from aminoplast resins, the total non-volatile solids content in the aqueous coating composition is from about 0.1 to about 19 %.

3. A process according to claim 2, wherein the epoxy resin used in part (A)(1) is a polymer of the diglycidyl ether of bis-phenol A with an epoxide equivalent weight from about 200 to about 1500, the aminoplast resins are melamine-formaldehyde resins, and the ratio of the content of non-volatile solids from melamine-formaldehyde resin to the solids derived from epoxy resin in said intermediate concentrate is from about 0.5 % to about 100 %.

4. A process according to claim 3, wherein the epoxy resin used in part (A)(1) has an epoxide equivalent weight from about 300 to about 1300, the ratio of the content of non-volatile solids from melamine-formaldehyde resin to the solids derived from epoxy resin in said intermediate concentrate is from about 1.0 % to about 75 %; and the ratio of the amount of component (A3) to the total of the amount of epoxy resin and amino-substituted carboxylic acids reacted to make the coating composition is from about 0.4 to about 5 %.

5. A process according to claim 4, wherein the epoxy resin used in part (A)(1) has an epoxide equivalent weight from about 445 to about 760, the ratio of the content of non-volatile solids from melamine-formaldehyde resin to the solids derived from epoxy resin in said intermediate concentrate is from about 2.0 % to about 36 %; the ratio of the amount of component (A3) to the total of the amount of epoxy resin and amino-substituted carboxylic acids reacted to make the coating composition is from about 1.1 to about 1.8 %, component (A3) includes both (i) a fluorinated surfactant consisting predominantly of fluorinated alkyl esters and (ii) a non-fluorine-containing ethoxylate of nonyl phenol with an average of about 9 ethylene oxide molecules per phenol molecule in a ratio of surfactant type (i) to the surfactant type (ii) that is from about 0.70 to about 0.95, and the total non-volatile solids content in the aqueous coating composition is from about 3.8 to about 5.2 %.

6. A process according to claim 5, wherein the aqueous coating composition contains silicone resin in an amount such that the ratio of the amount of silicone resin to the total of epoxy resin and substituted aromatic carboxylic acid condensed as recited in part (A1) is from about 0.0050 to about 0.0059.

7. A process according to claim 4, wherein the aqueous coating composition contains silicone resin in an amount such that the ratio of the amount of silicone resin to the total of epoxy resin and substituted aromatic carboxylic acid condensed to form the modified resin in part (A1) is from about 0.0045 to about 0.007.
- 5 8. A process according to claim 3, wherein the aqueous coating composition contains silicone resin in an amount such that the ratio of the amount of silicon resin to the total of epoxy resin and substituted aromatic carboxylic acid condensed as recited in part in part (A1) is from about 0.003 to about 0.01.
- 10 9. A process according to claim 2, wherein the aqueous coating composition contains silicone resin in an amount such that the ratio of the amount of silicon resin to the total of epoxy resin and substituted aromatic carboxylic acid condensed as recited in part in part (A1) is from about 0.001 to about 0.03.
10. A process according to claim 1, wherein the aqueous coating composition contains silicone resin.
- 15 11. A process according to claim 10, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 7.5 to about 13.5 and (A'') of rinsing the aqueous cleaning composition from the surface with water, wherein the mass per unit area of the coating formed is from about 100 to about 4000 mg/m².
- 20 12. A process according to claim 9, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 8.5 to about 13.0 for a time not greater than about 90 seconds and (A'') of rinsing the aqueous cleaning composition from the surface with water, wherein the surface to be coated is water-break-free after step (A'') and the mass per unit
- 25 area of the coating formed is from about 500 to about 1700 mg/m².

13. A process according to claim 8, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 9.0 to about 12.5 for a time not greater than about 75 seconds and (A'') of rinsing the aqueous cleaning composition from the surface with water, wherein the surface to be coated is water-break-free after step (A'') and the mass per unit area of the coating formed is from about 600 to about 1400 mg/m².

14. A process according to claim 7, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 9.5 to about 12.0 for a time not greater than about 60 seconds and (A'') of rinsing the aqueous cleaning composition from the surface with water, wherein the surface to be coated is water-break-free after step (A'') and the mass per unit area of the coating formed is from about 700 to about 1200 mg/m².

15. A process according to claim 6, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 10.0 to about 11.5 for a time not greater than about 40 seconds and (A'') of rinsing the aqueous cleaning composition from the surface with water, wherein the surface to be coated is water-break-free after step (A'') and the mass per unit area of the coating formed is from about 750 to about 1100 mg/m².

16. A process according to claim 5, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 9.5 to about 12.0 for a time not greater than about 60 seconds and (A'') of rinsing the aqueous cleaning composition from the surface with water, wherein the surface to be coated is water-break-free after step (A'') and the mass per unit area of the coating formed is from about 700 to about 1200 mg/m².

17. A process according to claim 4, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 9.0 to about 12.5 for a time not greater than about 75 seconds and (A'') of rinsing the aqueous cleaning composition from the surface with water, wherein the surface to be coated is water-break-free after step (A'') and the mass per unit area of the coating formed is from about 600 to about 1400 mg/m².

18. A process according to claim 3, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 8.5 to about 13.0 for a time not greater than about 90 seconds and (A'') of rinsing the aqueous cleaning composition from the surface with water, wherein the surface to be coated is water-break-free after step (A'') and the mass per unit area of the coating formed is from about 500 to about 1700 mg/m².

19. A process according to claim 2, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 7.5 to about 13.5 and (A'') of rinsing the aqueous cleaning composition from the surface with water, wherein the mass per unit area of the coating formed is from about 100 to about 4000 mg/m².

20. A process according to claim 1, said process comprising, before step (A), additional steps (A') of cleaning the surface to be coated with an aqueous cleaning composition having a pH from about 7.5 to about 13.5 and (A'') of rinsing the aqueous cleaning composition from the surface with water.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/15606

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B 05 D 1/38, 3/02, 3/10, 3/12, 7/16

US CL : 427/327, 388.4, 386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/ 318, 327,386,387,388.4, 410

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,098,744 (ALLEN ET AL) 04 July 1978, col.1, line 54-col.6, line 59; Examples.	1-4, 17-20
Y	US, A, 5,218,031 (NAYDER ET AL) 08 June 1993, col.3, lines 14-60; col.4, line 20-col.5, line 53; col.7, lines 49-55; col.8, lines 40-44; col.9, line 25-col.10, line 37; col.13, lines 40-68; col.16, lines 1-12.	1-4, 17-20
Y	US, A, 4,116,853 (BINNS) 26 September 1978, Fig., col.1, line 27-col.2, line 11.	17-20
A		11-16
A	US, A, 3,693,711 (ZYGIEL) 26 September 1972, col.3, line 20-col.4, line 37.	7-14

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:		*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
A	document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E	earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
O	document referring to an oral disclosure, use, exhibition or other means		
P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

18 MARCH 1996

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02 MAY 1996

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/15606

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,427,034 (NAGATA ET AL) 24 January 1984, col. 1, lines 10-20; col. 9, lines 51-61	7-14

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS

search terms: heat exchanger#, epoxy, wetting agent# or surfactant# or surface active agent#, water break, aluminum, silicone polymer# or silicone resin#, coat###; conductiv### or heat transfer or conductance